GB 0326927.1

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of:

MIDDLESEX SILVER CO. LIMITED,
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Incorporated in the United Kingdom,

[ADP No. 08940447001]

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	19NOV03 E853428-1 D01049 P01/7700 0.00-0326927.1
2. Patent application number *(The Patent Office will fill in this part)*	0326927.1
3. Full name, address and postcode of the or of each applicant *(underline all surnames)*	COLE, Paul, Gilbert Lucas & Co. 135 Westhall Road Warlingham Surrey CR6 9HJ
	SECTION 30 (1977 ACT) APPLICATION FILED 27/8/04
Patents ADP number *(if you know it)*	7928138001
If the applicant is a corporate body, give the country/state of its incorporation	
4. Title of the invention	SILVER SOLDER OR BRAZING ALLOYS AND THEIR USE
5. Name of your agent *(if you have one)*	COLE, Paul, Gilbert
"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	Lucas & Co. 135 Westhall Road Warlingham Surrey CR6 9HJ
Patents ADP number *(if you know it)*	05816709001

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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))*	Yes

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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	1+1
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11. I/We request the grant of a patent on the basis of this application.

Signature Paul Cole Date 19 Nov 03

Paul Cole

12. Name and daytime telephone number of person to contact in the United Kingdom

Paul Cole - 01883 626211

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SILVER SOLDER OR BRAZING ALLOY S AND THEIR USE

FIELD OF THE INVENTION

The present invention relates to silver solder or brazing alloys and to their use in making soldered joints in various grades of silver, particularly silversmithing grades. Silver brazing alloys are also known in the silversmithing trade as silver solders or solders and these terms are used interchangeably herein.

BACKGROUND TO THE INVENTION

Various silver-based alloys of the silver-copper-zinc type are useful as solders (brazing materials). Brazing has been defined as a joining process in which a filler metal is used which has a melting point of above 450°C, but below that of the parent metal and which is distributed in the joint by capillary attraction.

Silver, copper and zinc form a ternary eutectic with a silver content of 56% and melting at 665°C, see a ternary phase diagram which is given in Fig. 2 of Jacobson et al, *Development of new silver-free brazing alloys for steel tubular assembly*, supplement to the Welding Journal (sponsored by the American welding Society/Welding Research Council), August 2002, pages 149-S to 155-S downloadable from http://www.aws.org/wj/supplement/08-2002-JACOBSON-s.pdf,. A commercially supplied silver alloy recommended by the AWS for brazing mild steel or copper has the composition of 44 wt % Ag, 30 wt % Cu and 26 wt % Zn. Such an alloy has too low silver content for use in silversmithing, where solder alloys of at least 55 wt % Ag are the norm.

Depending on their melting temperatures, brazing alloys for use in silversmithing are classified as Easy, Medium and Hard, and the major UK suppliers quote the values below:

Thessco	Solidus	Liquidus
Easy	705°C	725°C
Medium	720°C	765°C
Hard	745°C	778°C

Johnson Matthey	Solidus	Liquidus
Easy	705°C	723°C
Medium	720°C	765°C
Hard	745°C	778°C

An alloy containing 75 wt % Ag, 22 wt % Cu and 3 wt % Zn is known and provides a good colour match for silver, but is high melting. An alloy with 70 wt % Ag, 20 wt % Cu and 10 wt % Zn is also of good colour and is lower melting, and a further alloy containing 65 wt % Ag, 20 wt % Cu and 15 wt % Zn is still lower melting, see http://www.wlv.com/joining/silvabrazrefchart.xls. This is, of course, only one web page from one of the various suppliers of solder alloys for silversmiths.

A corrosion-resistant silver solder for use in the electronics industry is disclosed in JP 61078592 (Kyocera) and is based on Ag, 0.05-19 wt %, Ge, 0.01-1.0 wt % Pd, and 0.01-2 wt % Li. An exemplified composition contains Ag 94 wt %, Ge 4 wt %, Pd 0.5 wt %, Li 0.5 wt %, Fe 0.5 wt % and Ni 0.5 wt %, and another exemplified composition has Ag 80%, Ge 11.95%, Pd 8% and Li 0.05%. Recommended amounts of germanium are relatively high. For silversmithing, the use of palladium is to be avoided, as is the use of lithium even in trace amounts. Although spreadability and wettability are said to be desirable properties, colour match to the material being soldered is not necessary.

Patent GB-B-2255348 (Rateau, Albert and Johns; Metaleurop Recherche) discloses a novel silver alloy that maintains the properties of hardness and lustre inherent in Ag-Cu alloys while reducing problems resulting from the tendency of the copper content to oxidise. The alloys are ternary Ag-Cu-Ge alloys containing at least

92.5 wt% Ag, 0.5-3 wt % Ge and the balance, apart from impurities, copper. Patents US-A-6168071 and EP-B-0729398 (Johns) disclose a silver/germanium alloy which comprises a silver content of at least 77 wt % and a germanium content of between 0.4 and 7%, the remainder principally being copper apart from any impurities, which alloy contains elemental boron as a grain refiner at a concentration of greater than 0 ppm. and less than 20ppm. Silver alloys according to the teaching of GB-B-2255348 and EP-B-0729398 are now commercially available in Europe and in the USA under the trade name Argentium (Ag 92.5 wt%, Cu 6.3 wt%, Ge 1.2 wt %), and the word "Argentium" as used herein refers to these alloys.

SUMMARY OF THE INVENTION

In one aspect the invention provides a silver solder alloy of the Ag-Cu-Zn family containing at least 55 wt % Ag and from 0.5 to 3 wt % Ge.

The above alloys can exhibit an advantageous combination of relatively low melting point, high flowability and good colour. In particular, such alloys may have a solidus temperature in the range of about 700 to about 750°C and a liquidus temperature in the range of about 725°C to about 780°C. They can be used for soldering or brazing jewellery metals including grades of silver such as Sterling. They are particularly advantageous for soldering Argentium silver.

Other preferred features of the invention will be apparent from the appended claims to which attention is directed. The alloys may contain 1.5-2.5 wt % Ge, especially 2.0-2.5 wt % Ge and more especially about 2.0 wt % Ge. Addition of Ge has been found to improve colour and reduce melting point as well as to increase corrosion resistance.

The Ag-Cu-Zn alloy typically contains 55-77 wt % Ag, 10-30 wt% Cu (preferably 56-75 wt %) and 8-15 wt % Zn. For flowability, it may further comprise 0.05-0.4 wt % Si especially about 0.1-0.2 wt % Si. Too large a proportion gives rise to brittleness. The alloy may further comprise 1-3 wt % Sn, especially about 2

wt % Sn which again reduces melting point and improves colour. It may further comprise an amount of boron of e.g. 1 ppm-0.3 wt % boron, and more typically 0.1-0.3 wt % of boron which reduces grain size and helps in rolling or drawing the composition.

Particular compositions comprise:

(a) 55-77 wt % Ag, 10-30 wt % Cu and 8-15 wt % Zn, 2-2.5 wt % Ge and 0.05-0.4 wt % Si,

(b) 55-77 wt % Ag, 10-30 wt % Cu and 8-15 wt % Zn, 2-2.5 wt % Ge and 1-3 wt % Sn, or

(c) 55-77 wt % Ag, 10-30 wt% Cu and 8-15 wt% Zn, 2-2.5 wt % Ge, 0.05-0.4 wt % Si and 1-3 wt % Sn.

The alloys of the invention may be provided any form that is convenient for silversmithing, e.g. rod, strip, wire, fine particles or a paste in which powdered metal is suspended in a vehicle, and may be used with conventional fluxes. In the case of pastes, US-A-5443658 (Hermanek) discloses a vehicle which is an aqueous gel containing 78 weight percent water, 10 weight percent mineral oil, 10 weight percent glycerin with the balance sodium carboxymethyl-cellulose. US-A-5120374 (Mizuhara) discloses gels containing 1-4 wt. % hydroxypropylcellulose, 40-80 wt. % 1,2-propanediol, 18-58 wt. % 2-propanol or 1-4 wt. % hydroxypropylcellulose, 20-70 wt. % 1,2-propanediol, 26-76 wt. % water. US-A-4475959 discloses an organic vehicle system based on resins dispersed in hydroxylic solvents. Low-melting hydrocarbon vehicles may also be used. Useful materials include those melting below room temperature to normally solid materials, e.g. C_{18}-C_{60} petroleum hydrocarbon waxes melting from 28°C. to 100°C. Such materials should have a low ash or solid residue content and either melt and flow, sublime and/or thermally decompose below 500°C. Useful hydrocarbons may be paraffinic, aromatic, or mixed aromatic paraffinic or mixtures of compounds of such characteristics, and include various mixtures of hydrocarbons, e.g., octadecane, mineral spirits, paraffin wax, and petrolatum (a colloidal system of non-straight-chain solid paraffinic

hydrocarbons and high boiling liquid paraffinic hydrocarbons, in which most of the liquid hydrocarbons are held inside the micelles), e.g., Vaseline.

The alloys can be used in any conventional soldering or brazing method c.g. using a hand torch, a fixed burner, induction or resistance heating or using a brazing furnace, preferably such a furnace which provides a protective atmosphere.

The invention is further illustrated in the following examples

Example 1

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	2.5%
Zn	-	14.5%
Si	-	0.1%
Cu	-	22.9%.

The resulting composition rolled well from cast ingot (satisfactory to 40% work hardened, then required annealing) and was evaluated as being a good solder when tested initially on gilding metal samples. The solder composition runs well along a 'T' join. Compared to known 56 and 60 silver solders (56 and 60 wt % Ag), the observed colour was good, and in particular it compared favourably to that of the 60 solder. On tarnish testing the present solder appeared brighter than the 56 and 60 solders. Its melting point on gilding metal using a Degussa flux was below that of the conventional 56 silver solder.

Samples of Argentium Ag/Ge supplied by Thessco Ltd of Sheffield were soldered using the above solder composition and the conventional 56 and 60 silver solder and using various fluxes:

Degussa Flux – the melting point of the above composition was slightly below that of the 60 silver solder. Beading of the solder was observed before dispersion. The resulting soldered joint exhibited good surface texture.

Superior 601 flux – The melting point of the above composition was lower than using the Degussa Flux and no beading of the solder was observed before dispersion. The resulting joint exhibited good surface texture.

Thessco Y Flux - The melting point of the above composition was lower than with either the Degussa Flux or the Superior 601 flux and was observed to be the same as the 56 silver solder No beading of solder before dispersion was observed, and the resulting soldered joint exhibited good surface texture when tested alongside the 60 silver solder but gave a slightly rough joint at the melting temperature of the 65 silver solder suggesting that a slightly higher temperature would be preferable.

The present solder was evaluated as being one of the best for use at relatively low temperatures Its advantages and disadvantages were as follows:

- Good colour in comparison to other lower M.P. solders including standard 56 silver solder.
- Lowest M.P. in comparison to the other solders produced.
- Solder runs well along a 'T' join.
- Good results in tarnish test carried out at Thessco Ltd. - the solder of this Example was brighter than both 56 and 60 solders after test.
- Surface of solder a little rough on some of the Argentium (Thessco) samples (soldering temperature may have needed to have been pushed a little higher with these samples).

Example 2

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	-
Zn	-	14%
Si	-	0.1%
Cu	-	25.9%

The resulting composition rolled well from cast ingot and provided a good solder that when tested on gilding metal samples was of good colour and ran well along a 'T' joint. However its melting point was above that of the 60 silver solder. When using Thessco F flux, beading of the solder before dispersion was observed, but the same beading occurred with the 60 silver solder.

Example 3

A brazing composition was prepared by melting together the following materials:

Ag	-	65%
Ge	-	2%
Sn	-	-
Zn	-	9%
Si	-	0.1%
Cu	-	23.9%

The resulting composition rolled well from cast ingot and provided a good solder when tested on gilding metal samples but its colour was slightly yellow. When using Thessco F flux, the melting point was slightly above that of known "Easy" silver solder and beading of the solder before dispersion was observed. Beading was also observed with Superior flux 6. Using Superior flux 601, the melting point was the same as that of Easy silver solder and beading of the solder before dispersion was not observed.

Example 4

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	-
Zn	-	14%
Si	-	0.4%
Cu	-	25.6%

The resulting composition rolled well from cast ingot and provided a good solder that when tested on gilding metal samples was of good colour. Its melting point was closely below that of the 60 silver solder. When soldered onto a flat surface of gilding metal, the surface texture exhibited was slightly rough.

Example 5

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	-
Zn	-	17%
Si	-	0.4%
Cu	-	24.6%

The resulting composition exhibited a yellow colour and was not evaluated further.

Example 6

A brazing composition was prepared by melting together the following materials:

Ag	-	56%
Ge	-	2%
Sn	-	-
Zn	-	19.8%
Si	-	0.2%
Cu	-	22%

The resulting composition exhibited a yellow colour and was not evaluated further.

Example 7

A brazing composition was prepared by melting together the following materials:

Ag	-	65%
Ge	-	2%
Sn	-	-
Zn	-	13.5%
Si	-	0.1%
Cu	-	19.2%

The resulting composition exhibited a yellow colour and the brazing beaded before dispersion.

Example 8

A brazing composition was prepared by melting together the following materials:

Ag	-	67%
Ge	-	2%
Sn	-	-
Zn	-	8%
Si	-	0.1%
Cu	-	22.9%

The resulting composition rolled well from cast ingot and provided a very good solder when evaluated using Thessco F flux on gilding metal samples. It exhibited good colour and no beading of the solder before dispersion. The composition exhibited a melting point slightly above that of Easy silver solder. However, when re-tested on Argentium Ag/Ge material (Thessco) using Degussa flux it exhibited a slightly better colour and a lower melting point than Easy silver solder. When soldering a 'T' joint in Argentium feeding the solder with a stick and using a Degussa flux the solder flowed very well. The present solder was judged to be one of the best for use at higher soldering temperatures because of the following advantages:

- Rolled well from cast ingot.
- M.P. slightly lower than that of Example 10
- Solder runs very well along a 'T' joint.
- Good colour.
- Good surface texture.

Example 9

A brazing composition was prepared by melting together the following materials:

Ag	-	60%
Ge	-	2%
Sn	-	-
Zn	-	13%
Si	-	0.1%
Cu	-	24.9%

The resulting composition rolled well from cast ingot and provided a very good solder when tested initially on gilding metal samples. It exhibited good colour and when using Degussa flux, no beading of the solder was observed before dispersing. Using Thessco F flux, beading of the solder before dispersion was observed, but known 60 silver solder also beaded on the same gilding metal sample. The above solder composition runs well along a 'T' joint and provides good surface texture. Its melting point is fractionally above that of known 60 silver solder When soldered onto Argentium (Thessco) the colour was fairly good and the solder appeared greyer than Easy solder.

Example 10

A brazing composition was prepared by melting together the following materials:

Ag	-	70%
Ge	-	2%
Sn	-	-
Zn	-	8%
Si	-	0.1%
Cu	-	19.9%

The resulting composition rolled well from cast ingot and provided a very good solder when evaluated initially on gilding metal samples. When using Degussa flux no beading of the solder was observed before dispersion, but beading was observed using Thessco F flux. The solder exhibited good surface texture and had a melting point slightly lower than Easy. When tested on Argentium (Thessco) using Degussa flux, its melting point was slightly higher than that of the solder of Example 8, but its colour was slightly better. The present composition was judged to be one of the best for use at higher soldering temperatures because of the following advantages:

- Rolled well from cast ingot.
- Good colour match with Argentium - slightly better colour than Example 8.

- M.P. slightly lower than Easy.
- Solder runs well along a 'T' joint.
- Generally good surface texture.

Example 11

A brazing composition was prepared by melting together the following materials:

Ag	-	56%
Ge	-	2%
Sn	-	-
Zn	-	13%
Si	-	0.2%
Cu	-	28.8%

The resulting composition rolled well from cast ingot and provided a good solder as evaluated on gilding metal samples, with good colour and good surface texture. The solder ran well along a 'T' join using Thessco flux. Also using Thessco flux, a large section of gilding metal spinning was soldered onto a base without any problems and with good solder flow. A sample was tested alongside 56 silver solder using different fluxes and was found to have a higher melting point. With Thessco F flux, both the present solder composition and the 56 silver solder exhibited beading before dispersion, whereas with Degussa flux beading results varied between samples.

Example 12

A brazing composition was prepared by melting together the following materials:

Ag	-	74%
Ge	-	2%
Sn	-	-
Zn	-	8%

Si	-	0.1%
Cu	-	15.9%

The resulting composition rolled well from cast ingot and provided a good solder as evaluated on gilding metal samples, with good colour and good surface texture. The solder ran well along a 'T' joint using Thessco flux. Its melting point was slightly lower than Easy silver solder and fractionally lower than the solder of Example 10. Using Thessco F flux, beading of the solder before dispersion was observed but the resulting joint had good surface texture. When tested on Argentium (Thessco) an excellent colour match was achieved and the same melting temperature as Easy silver solder was obtained but with incomplete dispersion, suggesting that a higher melting temperature is desirable.

Example 13

A brazing composition was prepared by melting together the following materials:

Ag	-	60%
Ge	-	3%
Sn	-	-
Zn	-	12%
Si	-	0.1%
Cu	-	24.9%

The resulting composition had a melting point lower than known 56 silver solder but did not roll well from cast ingot.

Example 14

A brazing composition was prepared by melting together the following materials:

Ag	-	60%
Ge	-	2.5%
Sn	-	-

Zn	-	12.5%
Si	-	0.1%
Cu	-	24.9%

The resulting composition rolled quite well from cast ingot (satisfactory to 40% work hardened, then required annealing).

Example 15

A brazing composition was prepared by melting together the following materials:

Ag	-	60%
Ge	-	2.5%
Sn	-	-
Zn	-	12.5%
Si	-	0.1%
Cu	-	24.9%

The resulting composition rolled quite well from cast ingot (satisfactory to 40% work hardened, then required annealing) and exhibited good colour. Samples tested on gilding metal alongside known 56 and 60 silver solders using different fluxes exhibited beading before dispersion.

Example 16

A brazing composition was prepared by melting together the following materials:

Ag	-	74%
Ge	-	2%
Sn	-	1%
Zn	-	7.5%
Si	-	0.2%
Cu	-	15.3%

The resulting composition rolled well from cast ingot and exhibited good colour but its melting point was higher than Easy solder and than the solder of Example 12, and it does not disperse fully.

Example 17

A brazing composition was prepared by melting together the following materials:

Ag	-	74%
Ge	-	2%
Sn	-	-
Zn	-	13%
Si	-	0.2%
Cu	-	10.8%

The resulting composition did not roll well from cast ingot. It was tested initially on gilding metal using Degussa Flux and exhibited better colour and a reduced melting point compared to Easy.

Example 18

A brazing composition was prepared by melting together the following materials:

Ag	-	74%
Ge	-	2%
Sn	-	-
Zn	-	13%
Si	-	-
Cu	-	11%

The resulting composition rolled quite well from cast ingot (satisfactory to 40% work hardened, then required annealing). Solder tested initially on gilding metal using Degussa flux exhibited good colour and a lower melting point than Easy silver solder. When tested on Argentium (Thessco) Ag/Ge material alongside

Easy silver solder, the present composition exhibited lower melting point and after polishing provided a better colour match to the Argentium, making the Easy silver solder look yellow. When tested on Argentium using Degussa flux alongside the solder of Example 10, the melting point was similar or slightly lower and the colour match after polishing was slightly darker. When tested on Argentium using Degussa flux, the solder ran well along a T-joint. The present solder was judged to be one of the best for use at higher temperatures for the following reasons:

- Solder does not contain Si (one less constituent to add to the alloy).
- M.P. fractionally lower than that of Example 10 (as seen with sample 2).
- Solder runs well along a 'T' joint.
- Good surface texture.
- Rolled well from cast ingot.

Example 19

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	2.5%
Zn	-	14.5%
Si	-	-
Cu	-	23%

The resulting composition was the same as Example 1 except that the silicon was omitted. It rolled quite well from cast ingot (satisfactory to 40% work hardened, then required annealing). When tested on Argentium (Thessco) material alongside 56 silver solder using Degussa flux, it ran well along a T-joint, exhibited a melting point slightly higher than 56 silver solder, and exhibited better colour. When tested on samples of Argentium (Thessco) alongside the solder of Example 1 using Degussa the melting point was unchanged, the colour became fractionally more yellow and the solder did not disperse so well.

Example 20

A brazing composition was prepared by melting together the following materials:

Ag	-	74%
Ge	-	2%
Sn	-	1%
Zn	-	11.4%
Si	-	0.2%
Cu	-	11.4%

The resulting composition was a very hard alloy, very brittle when rolled from cast ingot and yellow in colour in comparison to Easy silver solder.

Example 21

A brazing composition was prepared by melting together the following materials:

Ag	-	68%
Ge	-	2%
Sn	-	2%
Zn	-	8%
Si	-	0.1%
Cu	-	19.9%

The resulting composition rolled well from cast ingot, exhibited a melting point slightly lower than Easy silver solder, and good colour, although it was slightly more yellow than Easy silver solder.

Example 22

The brazing composition of Example 21 was re-melted with 3 wt % added tin. The resulting composition rolled not as well as that of Example 21: it rolls down to 40%

then becomes brittle. Its melting point was lower than the composition of Example 21, showing that addition of tin lowers the melting point, and its melting point was lower than that of 60 silver solder. Its colour was yellow compared to Easy solder, but it flowed well using F flux.

Example 23

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	1.4%
Zn	-	14.5%
Si	-	0.1%
Cu	-	24%

The resulting composition rolled better than the solder of Example 1, illustrating that tin additions tend to make silver solders harder and more brittle. When soldered onto gilding metal using Thessco F flux, the present composition had a melting point lower than 60 silver solder but beaded before dispersing. The 56 silver solder also beaded at the same time as the present solder but dispersed before the present solder. When soldered onto Argentium using F flux, the present solder dispersed well, melted fractionally below 56 silver solder and exhibited slightly better colour than that solder.

Example 24

A brazing composition was prepared by melting together the following materials:

Ag	-	69%
Ge	-	2%
Sn	-	2%
Zn	-	8%
Si	-	0.1%
Cu	-	18.9%

The resulting composition rolled well from cast ingot but melted at a temperature significantly higher than easy silver solder. When soldered onto Argentium (Thessco), both solders beaded before dispersion when heated from above but dispersed without beading when heated from below.

Example 25

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	2.5%
Zn	-	14.5%
Si	-	0.1%
B	-	0.14%
Cu	-	22.76%

The resulting composition (which was the same as that of Example 1 except for the addition of boron) rolled well from cast ingot (edge cracking at 64% reduction). When soldered onto Argentium (Thessco) using Thessco F flux it melted below 56 silver solder but higher than Thessco MX12 silver solder, exhibited similar colour to the solder of Example 1 and dispersed well. This solder

composition was evaluated as being one of the joint best for low temperature uses, and it had the following advantages:

- Addition of boron allows the alloy to roll better than the solder of Example 1.
- M.P. lower than 56 solder.
- Good colour in comparison to other lower M.P. solders including standard 56 silver solder.

A comparison of tarnish resistance was carried out using 'hard' and 'easy' silver solders together with the solder of this example (Y solder). Hard, Easy and Y solders were soldered onto Argentium Silver. The soldered samples were polished using two types of polishing compounds, then degreased using a solvent cleaner in an ultrasonic cleaning tank and finally wiped with a silver polishing cloth. An accelerated tarnishing procedure was carried out by exposing the samples to neat ammonium polysulphide solution - 20% for 10 minutes. After 10 minutes exposure, the Y solder showed superior tarnish resistance in comparison to both the hard and easy silver solders as shown in Fig. 1, which gives photographs of the samples.

Example 26

A brazing composition was prepared by melting together the following materials:

Ag	-	63%
Ge	-	2%
Sn	-	1%
Zn	-	14%
Si	-	0.1%
B	-	0.14%
Cu	-	19.76%

The resulting composition rolled well from cast ingot (edge cracking at 60% reduction) and when soldered using F flux onto Argentium (Thessco) had a melting point significantly lower than 60 silver solder. It exhibited a melting point between

the solders of Examples 10 and 25, a better colour than 56 or 60 silver solders and beading on one sample tested but not on the other. It was considered the best solder composition for use at medium temperatures because of its combination of rolling properties, melting point and colour.

Example 27

A brazing composition was prepared by melting together the following materials:

Ag	-	63%
Ge	-	2%
Sn	-	-%
Zn	-	15%
Si	-	0.1%
B	-	0.14%
Cu	-	19.76%

The resulting composition (which was the same as Example 26 apart from the absence of tin) rolled well from cast ingot (edge cracking at 75% reduction). When soldered onto Argentium (Thessco) using Thessco F flux it exhibited a melting point higher than that of the solder of Example 26, showing the effect of Sn in reducing the melting point.

Example 28

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	2.5%
Zn	-	14.5%
Si	-	-%
B	-	0.14%

Cu	-	22.86%

The resulting composition which was the same as Example 25 except for the absence of silicon) did not roll well from cast ingot (edge cracking at 32% reduction) and appeared yellow. It was believed that the mold temperature used was too yellow, and on re-melting with a higher mould temperature the resulting cast ingot rolled better with edge cracking at 57% reduction.

Example 29

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	2.5%
Zn	-	14.5%
Si	-	0.3%
B	-	0.14%
Cu	-	22.56%

The resulting composition rolled fairly well from cast ingot (edge cracking at 50% reduction).

CLAIMS

1. A silver solder or brazing alloy of the Ag-Cu-Zn family containing at least 55 wt % Ag and from 0.5 to 3 wt% Ge.

2. The alloy of claim 1, containing 1.5-2.5 wt % Ge.

3. The alloy of claim 1, containing about 2 wt % Ge.

4. The alloy of any preceding claim, containing 55-77 wt % Ag, 10-30 wt% Cu and 8-15 wt% Zn.

5. The alloy of any preceding claim, further comprising 0.05-0.4 wt % Si.

6. The alloy of claim 5, comprising about 0.1 wt% Si.

7. The alloy of any preceding claim, further comprising 1-3 wt % Sn.

8. The alloy of claim 7, comprising about 2 wt % Sn.

9. The alloy of any preceding claim, containing 55-77 wt % Ag, 10-30 wt% Cu and 8-15 wt% Zn, 2-2.5 wt % Ge and 0.05-0.4 wt % Si.

10. The alloy of any preceding claim, containing 55-77 wt % Ag, 10-30 wt% Cu and 8-15 wt% Zn, 2-2.5 wt % Ge and 1-3 wt % Sn.

11. The alloy of any preceding claim, containing 55-77 wt % Ag, 10-30 wt% Cu and 8-15 wt% Zn, 2-2.5 wt % Ge, 0.05-0.4 wt% Si and 1-3 wt % Sn.

12. The alloy of any preceding claim, further comprising 0.1-0.3 wt % boron.

13. The alloy of any preceding claim having a solidus temperature of about 705°C and a liquidus temperature of about 725°C.

14. The alloy of any of claims 1-12, having a solidus temperature of about 720°C and a liquidus temperature of about 765°C.

15. The alloy of any of claims 1-12, having a solidus temperature of about 745°C and a liquidus temperature of about 778°C

16. A silver brazing alloy substantially as described in any of the Examples.

17. Use of the alloy of any preceding claim to solder or braze a joint in silver.

18. Use of the alloy of any of claims 1-16 to solder or braze a joint in Sterling silver.

19. Use of the alloy of any of claims 1-16 to solder or braze a joint in silver of content about Ag 92.5 wt%, Cu 6.3 wt%, Ge 1.2 wt %.

20. An alloy according to any of claims 1-16, which is in the form of rod, strip or wire.

21. An alloy according to any of claims 1-16, which is in the form of paste.

ABSTRACT

SILVER SOLDER OR BRAZING ALLOY S AND THEIR USE

The present invention relates to silver solder or brazing alloys and to their use in making soldered joints in various grades of silver, particularly silversmithing grades. They alloys are of the Ag-Cu-Zn family containing at least 55 wt % Ag and from 0.5 to 3 wt% Ge. They can exhibit an advantageous combination of colour, flowability and corrosion resistance.

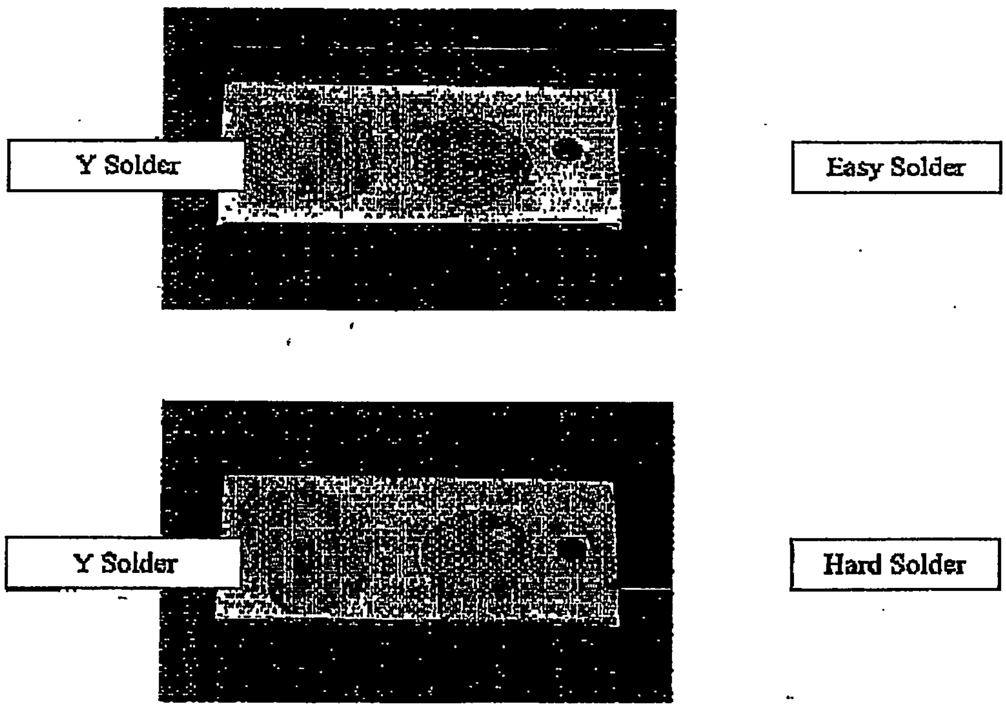

Fig. 1

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